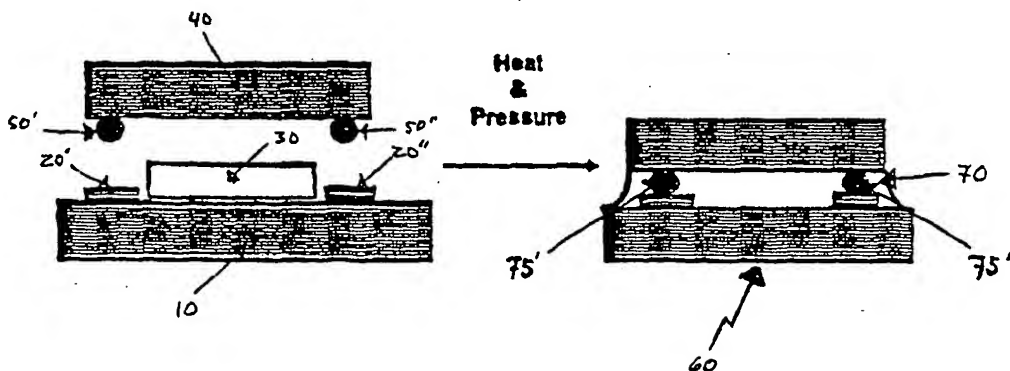




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(54) Title: UNDERFILL FILM COMPOSITIONS



(57) Abstract

A thin, uniform, high viscosity, uncured and unreinforced film (30) is disclosed. The film (30) comprises: (a) 0.5 to 50%, by weight of the film (30), of a polymeric or polymer forming matrix material; (b) 0.01 to 10%, by weight of the film (30), of a curing agent that is soluble in the matrix material at a temperature no greater than 100 °C; and (c) 50 to 80%, by volume of the film (30), of a substantially spherical and inert filler that has a maximum particle size no greater than 30 μm . The film (30) exhibits certain kinetic properties that permit it to cure very quickly and in a manner that does not produce void causing volatiles. The film (30) can be placed between a silicon chip (40) and a printed board (10) in a flip-chip assembly process and cured to form an underfill (70). The curing step can be conducted during the same heat cycle used to form the solder joints (75' and 75'') in the flip-chip process. Underfilled assemblies (60) created using said film (30) exhibit a thermal cycle resistance that is 250% greater than the obtained using traditional low viscosity underfill materials.

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UNDERFILL FILM COMPOSITIONS

Technical Field

This invention pertains to uncured and unreinforced, thin, uniform, high viscosity films. The films are capable of curing in a quick, steady and uniform manner to form void free, isotropic materials that exhibit exceptionally high thermal cycle resistance. More specifically, this invention relates to films for use in adhering and underfilling soldered chips to a printed board, methods for doing the same, and products generated thereby.

Background Art

Integrated circuit assemblies are utilized in virtually every electrical product ranging from computers to hair dryers. The basic components of an integrated circuit assembly are a printed board (PB) and a semiconductor chip.

A PB is a general term that embraces any printed wiring or printed circuit configuration. The term includes both rigid and flexible boards made from any organic or ceramic material. The term embraces single, double, and multilayer configurations. A printed wiring board (PWB) is a subset of PB which only contains printed point-to-point connections (wiring). A printed circuit board (PCB) is another subset of PB which contains printed components (circuits) as well as point-to-point connections (wiring). In the following description, any reference to a PB is intended to encompass both PWBs and PCBs.

Each semiconductor chip contains input/output points (I/Os), or leads, on its surface. These I/O's are connected to the wiring or circuit pattern on the PB at specific points on the PB called "lands."

For a long time, die mounting was the primary means for connecting the I/Os on the chips to the lands on the PB. In this process, the chip is positioned against the non-printed side of the PB, with the I/O's facing up. Wires are then run through holes in the PB to the printed side which contains the lands. One end of each wire is soldered to an I/O on the chip and the other end is soldered to a land. Finally, a plastic covering is molded over the entire assembly to protect both the chips and the wires from environmental damage. Die mounting has proven expensive, cumbersome, unreliable, time consuming and generates a bulky product. Therefore, the industry has turned to other approaches.

A popular alternative to die mounting is direct attachment by a technique called "flip-chip." In the flip-chip approach, solder bumps are placed over the I/Os on the chip. The chip

1 is then inverted and placed directly onto the printed side of the PB so that the solder bumps on
2 the I/O's align with the lands on the PB. Heat is then applied to reflow the solder, thereby
3 forming solder joints. In the final product, a gap remains between the chip and the PB due to
4 the height of the solder joints (hereafter referred to as "chip/PB separation").

5 Flip-chip is considered superior because all of the necessary interconnections are formed
6 simultaneously between the chip and the PB. In addition, the flip-chip approach frees up
7 enormous space on the PB for the attachment of many more chips. The additional space is due
8 both to the absence of bulky wires running through the PB and to the absence of the protective
9 coverings for these wires. Thus, use of the flip-chip process simplifies the manufacture of
10 integrated circuit assemblies and, additionally, enables the creation of smaller and more
11 powerful products.

12 However, a major disadvantage to flip-chip technology is that the solder joints are
13 susceptible to thermal stress and failure. The coefficients of thermal expansion (CTE) for the
14 chip, the PB, and the solder joint, are all different. These means that the materials swell and
15 contract at substantially different rates as the temperature rises and falls, thereby subjecting the
16 solder joints to stress. Over time the solder joints fatigue and fail. A failure in circuit continuity
17 can occur within as few as 50 thermal cycles. The term "circuit continuity" is defined herein
18 as a state wherein all of the circuit connections between the I/O's on a chip and the lands of a
19 PB are fully formed and unimpeded. The term "thermal cycle" is defined herein as a
20 temperature ramp that starts with a 30 minute plateau at -55°C, then rises to 125°C at a rate
21 sufficient to make the transition within 5 to 10 seconds, remains at 125°C for 30 minutes, and
22 then descends back to -55°C at a rate sufficient to make the transition within 5 to 10 seconds.

23 The industry has attempted to solve this CTE stress problem by filling the chip/PB
24 separation - a process called "underfilling." Generally, a low viscosity polymer or polymeric
25 composition is utilized. The term "low viscosity" as used in this application includes any liquid
26 or near liquid that possesses a viscosity that allows for complete underfilling of the flip-chip gap
27 in 60 seconds or less. In practice this viscosity appears to be 1000 poise or less at room

28 temperature, and 100 poise or less at an application temperature that is typically 45°C
29 but may be as high as 80°C. For example, a current liquid system (Dexter's FP4450) is 530
30 poise at room temperature and 40 poise at 40°C. Common low viscosity compositions are
31 epoxy, urethane, acrylic and silicon (STYCAR) resins, as well as bismaleimide fluids.

1 In this process, the low viscosity composition is dispensed onto two sides of the solder
2 bonded chip and "wicked" into the chip/PB separation at a controlled rate. The composition's
3 temperature may be increased a temperature between 70°C and 100°C to further reduce the
4 viscosity and thereby speed the wicking action. A current "fast flow" system has a spreading
5 rate of 2.5 to 3.0 cm per minute at 80°C. Once this flow is completed, the dispensing machine
6 is again used to apply the low viscosity composition to the remaining two sides of the chip. The
7 composition is then cured by heat or some other means so that it hardens into a protective
8 polymeric "underfill" (alternatively called an encapsulant or coupling agent). Typical "fast
9 cure" systems require 5 to 25 minutes at 150° to 165°C to cure. The cured composition serves
10 to insulate and protect the solder joints and enhances the bond between the chip and the PB.
11 As a result, survival periods of 2000 thermal cycles are not uncommon. The following
12 references are illustrative of the art of underfilling using low viscosity compositions, and known
13 variations thereof: (1) U.S. Patent No. 4,999,699; (2) U.S. Patent No. 5,089,440; (3) U.S.
14 Patent No. 5,203,076; (4) U.S. Patent No. 5,311,059; (5) U.S. Patent No. 5,385,869; (6) U.S.
15 Patent No. 5,442,240; (7) U.S. Patent No. 5,450,283; (8) U.S. Patent No. 5,647,123; (9) U.S.
16 Patent No. 5,654,801; and (10) U.S. Patent No. 5,681,757.

17 Unfortunately, the process of underfilling the chip/PB separation with a low viscosity
18 polymer or polymeric forming composition is not without problems. The following problems
19 exist:

20 First, most of the low viscosity compositions utilize anhydride hardening agents to form
21 a cured polymeric product, including the composition set forth in U.S. Patent No. 5,654,081 and
22 the compositions detailed in U.S. Patent Nos. 4,999,699 and 5,089,440. Anhydrides exhibit a
23 tendency to undergo hydrolysis into a diacid when subjected to environmental moisture. This
24 hydrolysis results in a subsequent performance reduction.

25 Second, considerable time is required to wick conventional low viscosity compositions
26 and the time required increases as the surface area of the chip increases. This is problematic
27 because, at the same time underfills have been finding success, the size and number of chips per
28 integrated circuit assembly have increased. In some leading edge applications, the chips are
29 now large enough and numerous enough to make wicked underfills impractical due to
30 subsequent production rate slowdowns.

1 Third, there is pressure to utilize smaller and smaller solder bumps in order to reduce
2 the number of shorts that occur in integrated circuit assemblies when a solder bump
3 unintentionally flows over more than one land. However, smaller solder bumps decrease the
4 chip/PB separation which hinders the ability of the low viscosity compositions to flow into
5 position and, thereby, creates voids. These voids trap moisture and create an environmental
6 hazard for the chip that eventually results in operational failure. To avoid this problem,
7 dispensing techniques often use additional processing steps to ensure that air pockets do not
8 form within the composition as it flows underneath the chip.

9 Fourth, considerable time is required to cure conventional low viscosity compositions.
10 Once again, the increased time is necessary in order to prevent voids which trap moisture within
11 the composition.

12 Fifth, the low viscosity compositions are not designed to cure simultaneously with the
13 solder bonding step that links the I/Os to the lands. The use of a two step process wherein the
14 solder bonding step is effected at one temperature, and the wicking and curing of the underfill
15 are effected at one or more additional temperatures, adds time and complication to the
16 manufacturing process.

17 Sixth, conventional low viscosity compositions are thixotropic, making consistent
18 dispensing of controlled volumes difficult. As a result conventional low viscosity compositions
19 have proven troublesome to control.

20 Seventh, wicking low viscosity compositions requires considerable space which
21 handicaps large scale manufacturing. Significant amounts of free room must be provided
22 around the perimeter of the chip in order to properly position the dispenser. This serves to delay
23 the positioning of other semiconductor chips in the vicinity.

24 Eighth, there are various secondary burdens and costs to wicking low viscosity
25 compositions that the industry would rather avoid. For instance, the dispensers containing the
26 low viscosity compositions must be cleaned after every use. This is time consuming.
27 Furthermore, the solvents utilized to clean the dispensers create environmental waste, the
28 disposal of which is heavily regulated and often costly.

29 Ninth and finally, relatively large thermal expansion differentials still exist in flip-chip
30 assemblies utilizing many of the low viscosity underfills. This is because the cured underfills

1 possess high CTEs in comparison to the solder joint. This problem is recognized in the
2 aforementioned U.S. Patent No. 5,654,081.

3 Therefore, there is a need in the industry for improved underfill compositions and
4 improved underfilling methods. One attempt to meet this need is set forth in U.S. Patent No.
5 5,386,624. U.S. Patent No. 5,386,624 teaches a method of mounting an electromechanical
6 device onto a substrate that comprises: (1) placing a pre-cut film between an electromechanical
7 device and a substrate; and (2) treating the film with heat, and optionally pressure, so that it
8 flows to fill all of the voids between the electromechanical device and the substrate. The
9 underencapsulant film is vaguely described as "a non-conductive resin or epoxy film."
10 Alternatively, "the underencapsulant may comprise other types of underencapsulant materials,
11 such as at least one of the following materials including urethane and silicone." However,
12 besides being short on detail regarding the types of materials that may be employed, the
13 reference fails to recognize the importance of cure kinetics in regulating the void content of the
14 cured underfill. Additionally, the reference fails to effects of filler volume fraction, geometry
15 and particle size on the electrical continuity of the solder joints.

16 **Summary of Invention**

17 The invention is directed to uncured films that have been developed to meet industry's
18 need for faster processing underfill materials. The guiding concept behind the invention is that
19 the time required to underfill a chip can be greatly reduced by using solid films that can be
20 placed between the chip and the PB, flowed to the edges of the assembly, and cured during the
21 soldering step.

22 The uncured films all comprise a polymeric or polymer forming matrix material, a
23 curing agent, and a filler. The matrix material is present in the amount of 0.5 to 50% by weight
24 of the uncured film and is, preferably, an epoxy resin, such as a blend of phenol novolac epoxy,
25 liquid bisphenol epoxy and solid bisphenol epoxy. The curing agent is present in the amount
26 of 0.01 to 10% by weight of the uncured film, and is soluble in the matrix material at a
27 temperature no greater than 100°C. The filler is present in the amount of 50 to 80% by volume
28 of the uncured film, and is substantially spherical, inert, and has a maximum particle size no
29 greater than 30 μm .

30 The uncured films are also defined by a number of important physical and kinetic
31 parameters. First, the films must have a smooth and uninterrupted surface. Second, the films

1 must have a uniform thickness of 5 mils or less with a deviation of ± 0.5 mils or less and a Cpk
2 higher than 1.0. Third, the films must possess a high viscosity, meaning that the viscosity is at
3 least 50,000 poise at room temperature. Fourth, the films must exhibit little to no tack so that
4 they may be die-cut and machine placed. Fifth, the films must exhibit sufficient flexibility to
5 be handled without breaking. Sixth, the films must possess an activation energy no greater than
6 300 KJ/mol. Seventh, and finally, the films must retain more than 50% of their theoretical heat
7 of reaction when tested at a heating rate of 200°C/min.

8 The aforementioned uncured films can be placed between a chip and PB, and then cured,
9 to form a product that adheres the chip to the PB and, simultaneously, fills the separation
10 between the chip and the PB without undermining the electrical continuity of the solder joints.
11 When the aforementioned uncured films are cured, they exhibit a number of beneficial
12 properties. For example, the cured films are void free, have a CTE between 20 and 25 ppm/°C,
13 and exhibit an isotropic modulus, fracture strength, CTE, and thermal conductivity. In addition,
14 the cured films can withstand more than 2,000 thermal cycles and as many as 5,000 thermal
15 cycles. This represents a 250% increase in thermal cycle resistance compared to conventional
16 processes wherein a low viscosity product is wicked into place.

17 **Brief Description of Drawings**

18 The preferred embodiments of the invention will be described in detail with reference
19 to the following figures, wherein like numerals refer to like elements, and wherein:

20 **FIG. 1** illustrates the underfilling process of the instant invention;

21 **FIG. 2** illustrates the desired geometry of a flip-chip underfilled assembly made in
22 accordance with the instant invention;

23 **FIG. 3** is a graph plotting heat of reaction versus the heat up rate for three epoxy resin
24 films utilizing three different curing agents;

25 **FIG. 4** is a graph plotting the heating rate of two films; and

26 **FIG. 5** is a graph illustrating the particle size distribution of two filler mixes.

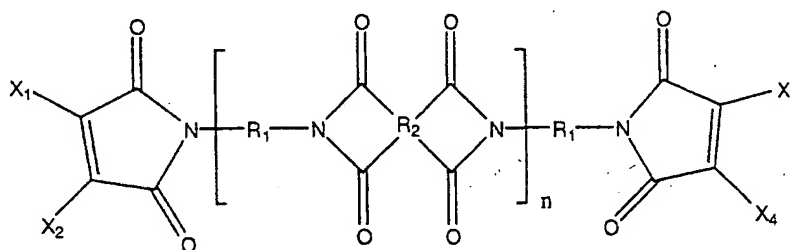
27 **Disclosure of Invention**

28 The invention is directed to uncured and unreinforced films that can be employed
29 between a soldered chip and a PB and cured to form an adhesive that binds the soldered chip
30 to the PB and, simultaneously, fills the separation between the soldered chip and the PB. Said
31 films comprise the following components: (a) a polymeric or polymer forming matrix material;

(b) a curing agent that is soluble in the matrix material at a temperature no greater than 100°C; and (c) a substantially spherical and inert filler that has a maximum particle size no greater than 30 μm .

The matrix material is present in an amount ranging from 0.5% to 50%, more preferably 2.5% to 15%, and most preferably 5% to 10%, based on the weight of the entire film. It is chosen from thermosetting or thermoplastic polymeric or polymer forming materials. Preferably, a thermosetting material is employed. Suitable materials include epoxy resins, cyanate ester resins, bismaleimide resins, vinyl ester resins, phenoxy resins, polyethersulfones, polyphenyleneoxides, polyesters, polyimides, polyamides (most notably nylons), and polyurethanes.

A preferred matrix material is a bis-maleimide (BMI) resin. BMI resins are also known as "polymerization of monomer reactants" (PMR) systems. BMI resins are formed by the reaction of an unsubstituted or substituted maleic anhydride, or a similar anhydride such as nadic



anhydride, with aromatic dianhydrides and aromatic diamines. Generally, BMI resins correspond to the following formula:

wherein R_1 may be any divalent organic radical, R_2 may be any tetravalent organic radical, X_{1-4} are, independently, any monovalent organic radical, and n is 0 or a positive integer of 1 to 20.

Preferably, R_1 is a substituted or unsubstituted phenyl, naphthalene, or diphenyl radical. If R_1 is a diphenyl radical then the two phenyl groups may be bonded directly together or bonded indirectly through a di- or higher valent organic radical such as an alkyl, alkene, carbonyl, oxygen, sulfur, sulfone, substituted or monosubstituted amine, organosilane, organosiloxane, organophosphite, and organophosphoryl unit.

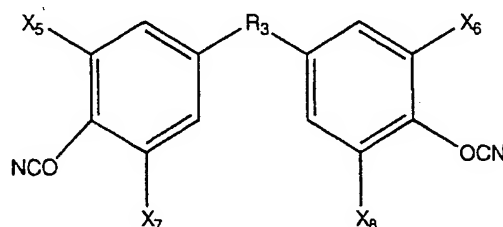
Preferably, R_2 is a substituted or unsubstituted phenyl, naphthalene, or diphenyl compound. Once again, if R_2 is a diphenyl radical then the two phenyl groups may be bonded

1 directly together or bonded indirectly through a higher valent organic radical such as an alkyl,
 2 alkene, carbonyl, oxygen, sulfur, sulfone, substituted or monosubstituted amine, organosilane,
 3 organosiloxane, organophosphite, and organophosphoryl unit.

4 As stated, the term BMI resins include resins according to the preceding formula
 5 wherein n equals zero. Suitable BMIs wherein n equals zero include the following: N,N'-p-
 6 phenylene-bis-maleimide; N,N'-m-phenylene-bis-maleimide; N,N'-4,4'-diphenylmethane-bis-
 7 maleimide; N,N'-4,4'-diphenylether-bis-maleimide; N,N'-4,4'-diphenylsulphone-bis-maleimide;
 8 N,N'-m-xylene-bis-maleimide; and N,N'-4,4'-diphenylcyclohexane-bis-maleimide.

9 The preferred BMI is PMR-15. PMR-15 is a reaction product of 4,4'-
 10 methylenedianiline, benzophenone, a dianhydride and nadic anhydride.

11 A second preferred matrix material is a cyanate ester resin. Cyanate ester resins
 12 comprise cyanate ester monomers and/or oligomers that have two or more cyanate ester (-OCN)
 13 functional groups per molecule. The molecular weight of cyanate ester monomers and
 14 oligomers typically ranges from 150 to 2000.



15 The cyanate ester resin preferably includes one or more bis-aryl cyanate esters having
 16 the general formula:

17 wherein R^3 is any substituted or unsubstituted, aliphatic, aromatic or cycloaliphatic structure
 18 including, but not limited to, linear and branched alkyls, sulfur, and fluorocarbons, and wherein
 19 $X_{5,8}$ are, independently, hydrogen or C_{1-4} alkyls.

20 Examples of suitable cyanate ester compounds include the following: 1,3 and 1,4
 21 dicyanatobenzene, 2-tert-butyl-1,4-dicyanatobenzene, 2,4-dimethyl-1,3-dicyanatobenzene, 2,5-
 22 di-tert-butyl-1,4-dicyanatobenzene, tetramethyl-1,4-dicyanatobenzene, 4-chloro-1,4-
 23 dicyanatobenzene, 1,3,5-tricyanatobenzene, 2,2- or 4,4-dicyanobiphenyl; 3,3',5,5-tetramethyl-
 24 4,4-dicyanobiphenyl; 1,3-, 1,4-, 1,5-, 1,6-, 1,8-, 2,6- or 2,7-dicyanatonaphthalene; 1,3,6-
 25 tricyanatonaphthalene; bis(4-cyanatophenyl)methane; bis(3,5-dimethyl-4-

1 cyanatophenyl)methane; 1,1-bis(4-cyanatophenyl)ethane; 2,2-bis(4-cyanatophenyl)propane; 2,2-
2 bis(4-cyanatophenyl)-1,1,1,3,3,3-hexafluoropropane; bis(4-cyanatophenyl)ether; bis(4-
3 cyanatophenoxyphenoxy)benzene; bis(4-cyanatophenyl)ketone; bis(4-cyanatophenyl)thioether;
4 bis(4-cyanatophenyl)sulfone; tris(4-cyanatophenyl)phosphite; and tris(4-
5 cyanatophenyl)phosphate.

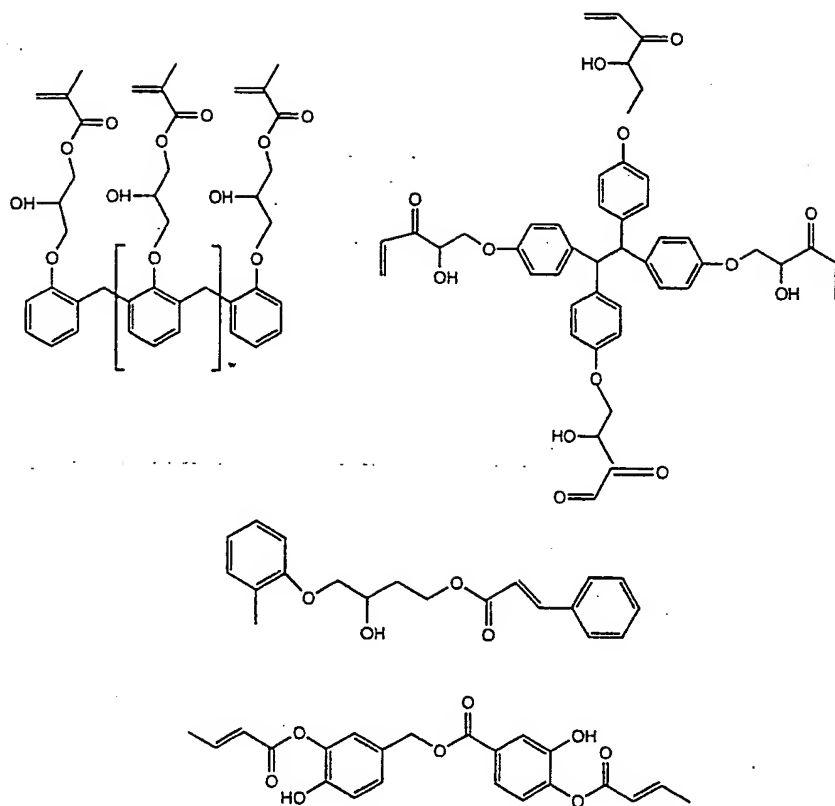
6 Also useful are cyanated novolac resins, cyanated bisphenol polycarbonate oligomers,
7 cyanato-terminated polyarylene ethers, dicyanate esters free of ortho hydrogen groups, mixtures
8 of di- and tricyanates, polyaromatic cyanates containing polycyclic aliphatic groups,
9 fluorocarbon cyanates and other cyanate derivatives.

10 A third preferred matrix material is an epoxy acrylate resin. Epoxy acrylate resins, or
11 vinyl ester resins as they are more commonly called, are produced by reacting an epoxy
12 compound with an ethylenically unsaturated acid such as acrylic acid, methacrylic acid, crotonic
13 acid and cinnamic acid. An alternative method of forming vinyl ester resins is to react glycidyl
14 (meth)acrylate with a multifunctional phenol. The most infamous of these materials is made
15 from the diglycidyl ether of bisphenol-A (DGEBA) and methacrylic acid.

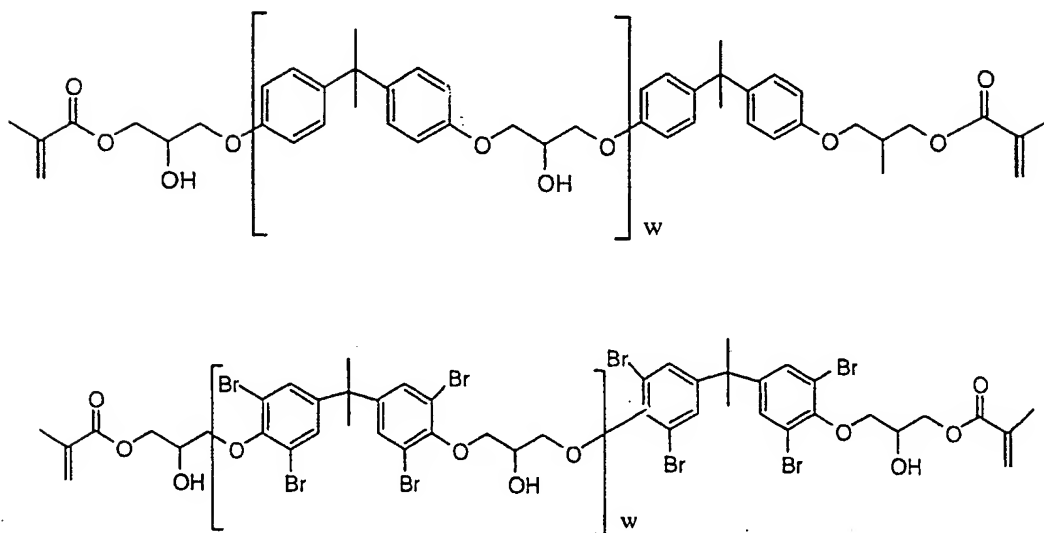
16 The epoxy compound is preferably an epoxy resin. Because of the variety of epoxy
17 compounds and unsaturated acids that may be employed, vinyl ester resins vary considerably
18 in viscosity, high-temperature properties and toughness. For example, vinyl ester resins
19 produced from novolac epoxy resins have better high-temperature properties than the DGEBA
20 based resins.

21 Examples of suitable vinyl ester resins include the following:
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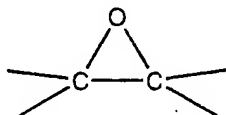
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In the above formulae, w is a positive value of from about 1 to about 20, preferably from about 2 to about 10.

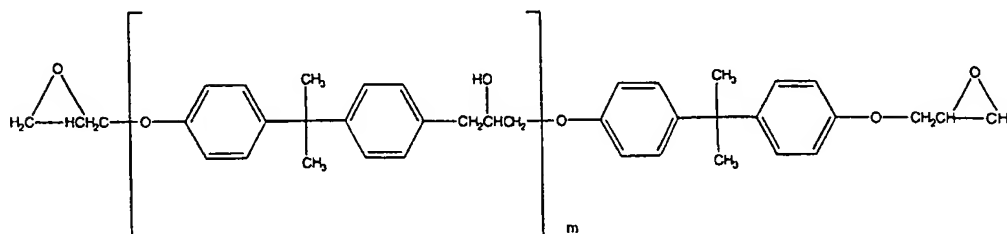
The vinyl esters resins may be used alone or in combination with monoethylenically unsaturated monomers, oligomers and polymers. Examples of suitable monoethylenically unsaturated monomers are styrene, o-methylstyrene, m-methylstyrene, p-methylstyrene, ethylstyrene, α -methylstyrene, m-methylstyrene, p-methylstyrene, ethylstyrene, α -vinyl-xylene, α -chlorostyrene, α -bromostyrene, vinylbenzylchloride, p-tert-butylstyrene, methyl methacrylate, ethyl acrylate, propyl acrylate, butyl acrylate, butyl methacrylate, propyl methacrylate, lauryl acrylate, 2-ethyl hexyl acrylate, ethyl methacrylate, diethylene glycol dimethacrylate, 1,4-divinylbenzene, and the like. Examples of suitable monoethylenically unsaturated oligomers and polymers are the reaction products of 2-hydroxyethylmethacrylate and various dianhydrides such as pyromellitic dianhydride benzophenone dianhydride.

A fourth preferred matrix material, and in fact the most preferred matrix material, is an epoxy resin. Epoxy resins are characterized as having two or more three membered rings, known as epoxy, epoxide, oxirane, or ethoxylene groups, that have the following structure:



The resin backbone may be aliphatic, cycloaliphatic, or aromatic, but is preferably aromatic. Epoxy resins are thermosetting resins that react with curing agents to yield insoluble and infusible three dimensional networks. Generally these resins have a theoretical heat of reaction ranging from 20 to 25 Kcal/eq when measured at 10°C/min using a DSC.

Epoxy resins are prepared by the reaction of active hydrogen containing compounds with an epihalohydrin followed by dehydro-halogenation. The simplest epoxy resin is prepared by the reaction of a bisphenol, such as bisphenol A, with an epichlorohydrin to form a diglycidyl ether of bisphenol A (DGEBA). A DGEBA has the following formula:



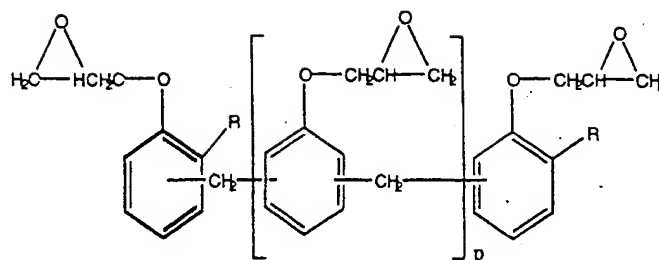
1 The value of m varies from 0 to about 30. Epoxy resins can be obtained in either liquid or
2 solid states.

3 Liquid states are obtained by reacting an active hydrogen containing compounds with
4 an excess of epihalohydrin in a caustic soda solution or other equivalent basic medium. The
5 ratio of active hydrogen containing compound to epihalohydrin in the formation of liquid
6 epoxy resins is generally 10:1, respectively. An excess of epihalohydrin is used in order to
7 minimize polymerization of the reactants to higher molecular weight species. In example,
8 the reaction of epichlorohydrin and bisphenol A in a 10:1 ration in the presence of caustic
9 soda would yield a liquid epoxy resin in accordance with the preceding formula wherein m
10 is nearly zero (around 0.2).

11 Solid epoxy resins are obtained by reacting an active hydrogen containing
12 compounds with epihalohydrin in theoretical molar ratio with little excess epihalohydrin.
13 Once again a caustic soda or equivalent basic medium is utilized. In example, the reaction
14 of epichlorohydrin and bisphenol A is a 1:1 ratio in the presence of caustic soda would yield
15 a high molecular weight solid epoxy resin in accordance with the preceding formula wherein
16 m is ranges from 2 to about 30.

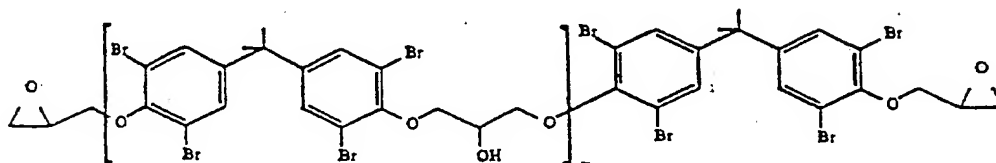
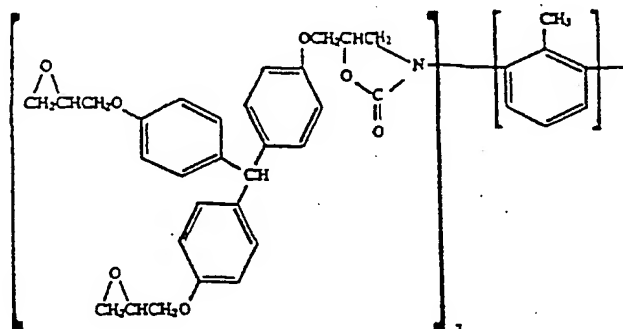
17 Epoxy resins include numerous modified adducts. This adducts are formed by
18 further reacting the epoxy resins with comonomers and copolymers including vinyl
19 compounds, acrylics, bis-aryl cyanate esters, polyesters, phenol and/or cresol novolacs, bis-
20 [4(2,3-epoxy propoxy)phenyl]methane, carboxyl rubbers and amines. The most
21 predominant adducts are epoxy-carboxyl rubber adducts, epoxy-amine adducts and epoxy
22 phenol novolac resins (EPNs).

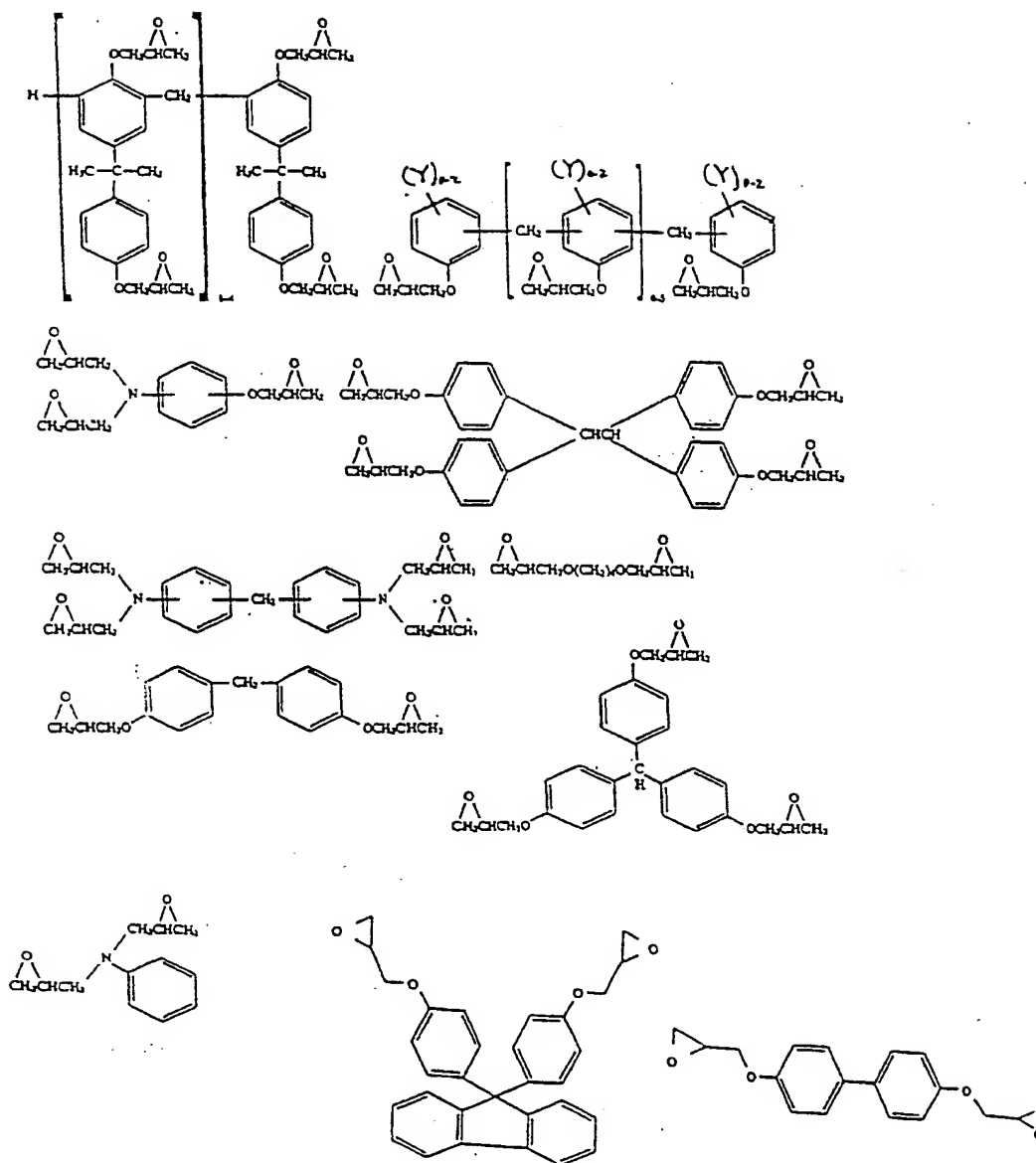
23 EPNs are made by glycidylation of an acid catalyzed condensation product of a
24 phenol and excess aldehyde. The product has random ortho- and/or para- methylene
25 bridges. The phenol may be chosen from any known member of the phenol group however
26 the compounds phenol and cresol are preferred. When cresol is used the adduct is called an
27 epoxy cresol novolac (ECN). EPNs and ECNs have the following structure:



1 wherein R is a hydrogen for EPNs and methyl for ECNs, and p is greater than or equal to
2 zero. The simplest EPN is bisphenol F.

3 Other suitable epoxy resins include those represented by the following formulae and
4 similar compounds:





wherein Y_{0-2} are, independently, any organic radical.

1 The most preferred epoxy resin comprises a blend of the following components: (1)
2 an epoxy phenol novolac, (2) a liquid bisphenol epoxy; and (3) a solid bisphenol epoxy. A
3 blend of these three components produces superior tack, drape, flow, and void resistance
4 compared to conventional underfill materials.

5 In the aforementioned blend, the epoxy phenol novolac is present in an amount of 1
6 to 50%, and most preferably 20 to 30% based on the weight of the non filler portion of the
7 underfill composition. Any phenol, aldehyde and epoxy functional compound may be
8 utilized to form the epoxy phenol novolac, but the preferred phenol is cresol, the preferred
9 aldehyde is formaldehyde and the preferred epoxy functional compound is epichlorohydrin.
10 The phenol, aldehyde and epoxy functional compound are reacted in a weight ratio of
11 3.6/1.0/3.1, respectively.

12 In the aforementioned blend, the liquid bisphenol epoxy is present in an amount of
13 1% to 50%, and most preferably 35 to 45% based on the non-filler portion of the underfill
14 composition. Any epoxy functional compound and bisphenol may be employed to form the
15 liquid bisphenol epoxy but the preferred epoxy functional compound is epichlorohydrin and
16 the preferred bisphenol is bisphenol A in a ratio ranging from between 2:1 to 20:1,
17 respectively.

18 In the aforementioned blend, the solid bisphenol epoxy is present in an amount of
19 1% to 30%, and most preferably 12% to 17% based on the non-filler portion of the underfill
20 composition. Any epoxy functional compound and bisphenol can be reacted to form the
21 solid bisphenol epoxy but the preferred epoxy functional compound is epichlorohydrin and
22 the preferred bisphenol is bisphenol A in a 1:1 to 1:2 ratio, respectively.

23 The second component in the uncured film is one or more curing agent/catalysts. In
24 thermosetting systems the curing agents are also known as hardening agents because they
25 cause the formation of a hard infusible product. Typically, the curing agents are utilized in
26 an amount ranging from 0.01 to 10% by weight of the film.

27 The curing agent must be soluble in the matrix material at a temperature less than or
28 equal to 100°C, and preferably is completely soluble in the matrix material at room
29 temperature. The solubility of the curing agent in the matrix material is important because
30 the diffusion kinetics of insoluble cure catalysts are much slower than their curing kinetics.

1 This results in the formation of a gel layer around the catalyst that hinders its dispersion and,
2 thereby hinders its ability to cause a quick, steady and uniform cure.

3 Virtually any conventional class of curing agent may be employed as long as it is a
4 species that is soluble in the matrix material at a temperature less than or equal to 100°C. As
5 stated, the preferred matrix materials include: (a) bismaleimide resins; (b) cyanate ester
6 resins; (c) vinyl ester resins; and epoxy resins. The following is a discussion of conventional
7 curing agents employed in each of the aforementioned preferred matrix materials:

8 BMI resin curing agents include: alkali metal salts of monocarboxylic acids,
9 dicarboxylic acids, cyanides or carbonates; secondary, tertiary and quaternary amines;
10 organophosphine and organophosphonium compounds; and peroxyketal compounds. BMI
11 resins may be reacted with amines, sulphides and adoximes to form extended polymer
12 structures. In the case of a bismaleimide-amine reaction, if the reaction is carried out with a
13 deficiency of amine, the polymer will have terminal double bonds which can be further
14 crosslinked with a multiunsaturated isocyanate. Typical multiunsaturated agents include
15 divinyl benzene and triallyl isocyanate.

16 Catalysts for the reacting the cyanate ester include metal salts such as zinc octoate
17 and cobalt naphthanate, amines, and organometallic compounds such as cyclopentadienyl
18 iron dicarbonyl dimer $[(C_5H_5Fe(CO))_2]$ and cyclopentadienyl manganese tricarbonyl
19 $[C_5H_5Mn(CO)_3]$.

20 Vinyl esters are polymerized by a free radical reaction that is usually initiated by a
21 thermal or catalytic decomposition of peroxides or a decomposition of a photoinitiator.
22 Illustrative of typical curing agents in the art are the following: benzoyl peroxide; dicumyl
23 peroxide; methyl ethyl ketone peroxide; ditertiary butyl peroxide; tertiary butyl
24 hydroperoxide; tertiary butyl perbenzoate; Luperoxi 118 (sold by Wallace and Tieman,
25 Lucidol Division, 1740 Military Road, Buffalo, N.Y. 14240); cumene hydroperoxide; or
26 other peroxides or a mixture thereof. It is common to combine metal salts of naphthenates,
27 e.g. cobalt naphthenate, and the like, and tertiary amines, such as dimethyl aniline, with the
28 peroxidic curing agent. The amount of curing agent is typically less than about 10 weight
29 percent of the resin formulation. Preferably, the curing agent ranges from about 0.1 to about
30 8 weight percent of the resin formulation.

1 Epoxy resin curing agents are either catalytic or coreactive. A catalytic curing agent
2 functions as an initiator for the epoxy resin polymerization, whereas a coreactive curing
3 agent acts as a comonomer in the polymerization process. The catalytic curing agents
4 include Lewis acids, Lewis bases and tertiary amines and may function by either an ionic or
5 cationic mechanism. The coreactive curing agents include active hydrogen containing
6 compounds such as primary and secondary amines, phenols, phenoplasts, aminoplasts,
7 alcohols, thiols, carboxylic acids and carboxylic anhydrides. Except for acid anhydrides,
8 these active hydrogen containing compounds leave pendant hydroxyl groups in the cured
9 resins.

10 Common epoxy resin curing agents include anhydrides, imidazoles, and diamides
11 and diamines such as dicyandiamide, m- and p-phenylenediamine, 4,4'-methylenedianiline,
12 3,3'-diaminodiphenyl sulfone (3,3'-DDS) and 4,4'-diaminodiphenyl sulfone (4,4'-DDS).
13 The amount of the coreactive curing agent used in an epoxy resin is generally such that one
14 curing agent reactive group is present per epoxy group.

15 It should be noted that anhydrides are not preferred curing agents. Anhydrides easily
16 undergo hydrolysis to diacid when subjected to environmental moisture resulting in
17 significant performance reduction. However, it is possible to synthesize anhydrides for this
18 application that would be useful.

19 Preferred epoxy resin curing agents for use in the invention are selected from the
20 group consisting of imidazoles, imidazole salts, primary and secondary amines, tertiary
21 amines, "urons" (dimethylamine-aromatic amine ureas), novolac resins and boron
22 compounds. More preferably, the curing agents are selected from liquid imidazoles. Most
23 preferably, the curing agents are chosen from the group consisting of 1-benzylimidazole,
24 2-ethyl-4-methylimidazole, 1-cyanoethyl-2-ethyl-4-methyl imidazole, 1-methylimidazole, 1-
25 heptadecylimidazole and phenylimidazole. The total amount of preferred curing agent
26 utilized is 0.01 to 0.1 moles of imidazole per equivalent of epoxy (M/eq), preferably 0.025
27 to 0.075 M/eq, and most preferably 0.06 to 0.07 M/eq.

28 The third component of the uncured film is one or more fillers that are inert and
29 insoluble in the matrix material. The objective is to include as high a volume fraction of
30 filler as practically possible, as this reduces the coefficient of thermal expansion in the final
31 cured film. The level of stress in the bonds formed between the chip and the PB is a

1 function of the difference in CTE between the solder bonds, the I/O's, the bonding lands, and
2 the cured underfill. A lower adhesive CTE reduces this difference and produces lower
3 levels of thermal stress and, consequently, improved durability.

4 In order to obtain a sufficiently high volume fraction, the filler needs to be
5 substantially spherical. The term "substantially spherical" is intended to convey the fact that
6 the particles are chosen from those fillers generally referred to as "spheres" in the art while,
7 at the same time, recognizing that there is really no such thing as a perfectly spherical
8 particle. Theoretically, the maximum volume fraction possible is on the order of 63%
9 for a uni-modal distribution of filler, 73% for a bi-modal distribution, and approximately
10 80% for a tri- or higher modal distribution. However, formulations containing the
11 maximum amount of filler are not practical because the viscosity of the resulting mixture
12 often becomes too high. As a result, practical formulations are usually 3 to 10% v/v lower
13 than the theoretical maximum. Therefore, the filler should be present in a volume fraction
14 of from 50 to 80%, preferably 60 to 75%, and most preferably 63 to 72%. Volumes less
15 than 50% will not provide a sufficiently low CTE.

16 It has been found that the maximum particle size of the filler component is critically
17 related to the ability to obtain and maintain 100% electrical continuity within all of the
18 circuit connections during the underfilling process. The particle size distribution is chosen
19 so that the film flows around and between the forming solder joints when heated and does
20 not get caught under or between the descending solder balls. The solder balls must be able
21 to push the filler away from the solder joint area.

22 The required maximum particle size is best defined in terms of the ratio between the
23 maximum particle size to the solder bump gap or chip/PB separation distance (d/s). The d/s
24 ratio is $1/2$, preferably $1/4$ and most preferably $1/10$. A d/s ratio of less than or equal to $1/2$
25 prevents the filler from getting caught under the solder or jamming between the solder
26 bumps. Typically, the solder bump spacing is $25\mu\text{m}$. Therefore, the maximum particle size
27 is typically no greater than $12.5\mu\text{m}$, preferably no greater than $8.25\mu\text{m}$, and most preferably
28 no greater than $2.5\mu\text{m}$. Microscopic examination shows that larger filler particles get
29 trapped at or near individual solder bumps, precluding bonding of these bumps to the
30 associated PB bonding land. These portions of the circuits, of course, do not exhibit any
31 electrical continuity. In contrast, microscopic examination shows that fillers that fall within

1 the aforementioned particle size parameters flow around and away from the solder bumps,
2 allowing all of the solder joints to be successfully bonded.

3 In general, to reduce thermal stress in the cured bond, the filler's CTE should be as
4 low as possible - and certainly less than 10 ppm/°C. The filler may be inorganic or organic.
5 Non-limiting examples of inorganic spherical filler are amorphous silica, alumina (Al_2O_3),
6 ceramic microspheres, (i.e. the Zeospheres produced by Zeeland corporation), and solid and
7 hollow glass spheres. Organic spheres can be formed from cured and crosslinked rubber and
8 thermoset resins as well as thermoplastic polymeric materials. Such fillers may have a
9 coating on their surface to maximize thermal conductivity. Silica is the preferred filler
10 because of its low coefficient of thermal expansion, its spherical shape, and the fact that it is
11 commercially available in several particle size distributions.

12 A number of other additives can also be present in the uncured film. Preferred
13 additives include, but are not limited to, tougheners, colorants, processing aids, thixotropic
14 compounds, internal mold release agents, and minor amounts of a temperature expandable
15 filler.

16 Acceptable tougheners include high molecular weight reactive resins, core/shell
17 rubbers and other soluble and reactive rubber materials. The tougheners may be used alone
18 or in combination. Two preferred tougheners are a high weight average molecular weight
19 Bisphenol A epoxy resin sold under the Trademark PHENOXY PKHH (Phenoxy
20 Associates) and a particulate silicone rubber sold under the Trademark X5-8452 (Dow
21 Corning). These tougheners improve the crack resistance of the cured underfill and play a
22 role in raising the thermal cycle resistance of the cured underfill. The total amount of
23 toughener utilized in the underfill is 0 to 20%, preferably 2.5 to 15%, and most preferably 10
24 to 15%, based on the non-filler portion of the underfill composition.

25 If colorants are used, they are selected from both soluble dyes and insoluble organic
26 and inorganic pigments. A preferred colorant is the blue phthalocyanine pigment sold as a
27 dispersion in epoxy resin as PDI 22-38010 by the Ferro Corporation. Such colorants are
28 added to aid machine optical recognition characteristics during underfilling operations. The
29 total amount of colorant dispersion utilized in the underfill is 0 to 7.5%, preferably 0.5 to
30 5% and most preferably 1.0 to 3.0 %, based on the non-filler portion of the underfill
31 formulation.

1 Acceptable processing aids include wetting agents, manufacturing aids, bubble
2 breakers and surfactants. The total amount of processing aid utilized in the underfill is 0 to
3 1.0%, preferably 0.01% to 0.5%, more preferably 0.1% to 0.25%, and most preferably
4 0.12%. Wetting agents are added to aid both the dispersion of the filler materials into the
5 resin and to release air included into the system by the addition of the filler. Manufacturing
6 aids are added to the formulation to support quality assurance audits of system composition
7 during the manufacturing process. Preferred processing agents include a polymeric acrylic
8 material sold under the Tradename of PC-1344 (Monsanto).

9 Acceptable thixotropic compounds include, but are not limited to, pyrogenic silicas,
10 clays and both organic and inorganic fibrous materials. A preferred thixotrope is Pyrogenic
11 silica. Thixotropic compounds are added to modify and control behavior of the underfill
12 formulation and to retard the separation and setting of the filler materials. The total amount
13 of thixotrope utilized in the underfill is 0 to 10%, preferably 0.5 to 5%, and most preferably
14 1 to 3% of the non-filler portion of the underfill formulation.

15 Acceptable internal mold release agents include, but are not limited to, natural and
16 synthetic waxes. Internal mold release agents serve to reduce the environmental moisture
17 adsorption at the air/underfill interfaces. The total amount of internal mold release agent is
18 0 to 5%, preferably 0.25 to 2.5%, and most preferably 0.5 to 1% of the non-filler portion of
19 the underfill formulation.

20 Acceptable temperature expandable fillers include those materials which possess
21 hollow thermoplastic shells containing a low molecular weight organic liquid therein, such
22 as a propellant. Typical shell materials include, but are not limited to polyvinyl chloride,
23 polyacrylonitrile and their copolymers thereof. Temperature expandable fillers serve to
24 reduce the dielectric constant of the cured underfill. The total amount of temperature
25 expandable filler utilized in the underfill is 0 to 15%, preferably 1 to 10%, and most
26 preferably 5 to 10% by weight of the total underfill.

27 In addition, to the aforementioned required and optional components, the uncured
28 film must comply with certain physical and kinetic parameters. The film must contain a
29 smooth, uninterrupted surface. It must have a uniform thickness of 5 mils or less with a
30 deviation of ± 0.5 mils or less and a Cpk higher than 1.0. The film must have a viscosity of
31 at least 50,000 poise at room temperature. It must exhibit sufficiently low tack to permit

1 die-cutting and machine placement and sufficient flexibility to be handled without breaking.
2 The film must have an activation energy no greater than 300 KJ/mol. Finally, the film must
3 retain more than 50% of its theoretical heat of reaction when tested a heating rate of
4 200°C/min.

5 The film must have a smooth and uninterrupted surface. Any interruption or pocket
6 on the surface of the film can trap air which may form voids at the surface when the film
7 melts and cures. These voids reduce adhesion and trap water vapor and other environmental
8 hazards

9 The film also must have a consistent and low film thickness 5 mils or less with a
10 deviation of ± 0.5 mils or less and a process capability index (Cpk) higher than 1.0. Cpk
11 measures the ability to create a product within specified limits. A Cpk greater than 1.0
12 means that there is a 99.9% chance that every area of the film is within the prescribed limits.
13 Preferably, the film thickness is 2-4 mils and most preferably 3-4 mils. Such requirements
14 regarding the thickness and uniformity of the film are necessary to ensure that the film can
15 be utilized to fill the thin chip/PB separation and provide enough resin to fillet around the
16 edges of the chip.

17 The film must have a viscosity of at least 50,000 poise at room temperature.
18 Generally, these high viscosity films also have an uncured glass transition temperature in the
19 range of 25°C to 40°C. The high viscosity of the inventive films is an essential difference
20 between the prior art relating to liquid underfills and the invention. The high viscosity
21 diminishes the tack of the film permitting die cutting and mechanical placement. It also
22 prevents resin creep and the resulting shape distortion. Furthermore, the high viscosity
23 allows the film to remain in one plane without breaking during placement.

24 The kinetics of the film's cure are critical to its success. A successful film must cure
25 completely during the soldering cycle utilized to attach the I/O's on the chip to the PB in a
26 steady manner that does not generate voids in the cured product. Typical soldering cycles
27 last 30 seconds at temperatures ranging from 200°C to 325°C. The heating rates used in
28 these processes are often greater than 600°C/min. It has been discovered that the void
29 content is controlled by the cure kinetics of the film. In order to form a void free product
30 under the aforementioned curing conditions, the film must have an activation energy that is
31 less than 300 KJ/mol, preferably less than 225 KJ/mol, and most preferably less than 200

1 KJ/mol, as defined by analysis of DSC curves at 10°C/min. In addition, the film must retain
2 greater than 50%, preferably greater than 65%, and most preferably greater than 70%, of its
3 theoretical heat of reaction, as measured using a DSC cure scan at 10°C/min, when tested at
4 a heating rate of 200°C/min. In the case of epoxy resins, the theoretical heat of reaction is
5 around 25 Kcal/eq.

6 Most prior art underfill compositions, such as the conventional wicked low viscosity
7 epoxy resins, do not meet the aforementioned kinetic limitations. As a result, these prior art
8 systems boil at temperatures less than the soldering temperature and gross void formation
9 occurs via resin evaporation. The voids, in turn, trap moisture from the air which inevitably
10 causes the chips to fail.

11 The uncured film is not reinforced. By this it is meant that there are no scrim fabrics
12 or other reinforcing materials either within, or adjacent to, the film during application. The
13 presence of any such reinforcing material during application would interfere with the solder
14 joint formation.

15 However, the uncured film may be sold in a form that is reinforced. More
16 specifically, the film may be positioned adjacent to one or more release liners. The liners
17 provide a protective support for the film during storage and are peeled away from the film
18 immediately prior to application. The release liners may be selected from a wide variety of
19 materials including metal foil, plastics such as polyethylene, polypropylene, polyester, and
20 the like, and paper. The release layers may be coated to aid separation from the film.

21 The aforementioned uncured film can be placed between a chip and PB, and then
22 cured, to form a product that adheres the chip to the PB and, simultaneously, fills the
23 separation between the chip and the PB without undermining the electrical continuity of the
24 solder joints. When the aforementioned uncured film is cured, it exhibits a number of
25 beneficial properties. For example, the cured film is void free, has a CTE between 20 and
26 25 ppm/°C, and has an isotropic modulus, fracture strength, CTE and thermal conductivity.
27 In addition, the cured film can withstand more than 2,000 thermal cycles and often can
28 withstand 5,000 thermal cycles. A thermal cycle resistance of 5,000 thermal cycles is a
29 250% increase compared to conventional processes wherein a low viscosity product is
30 wicked into place and cured.

1 A typical underfill process employing the films of this invention is set forth in **FIG.**

2 1. In **FIG. 1**, a PB 10 containing two or more bonding lands 20' and 20'' is placed on a
3 surface. The PB 10 is formed from a nonconductive substance which may comprise
4 compounds such as reinforced polyimides, reinforced polyesters, fluoropolymers, paper
5 phenolics such as NEMA-XXP, KAPTON, Teflon film, silicone rubbers, epoxies and
6 ceramic materials. On the surface of the PB 10 are point-to-point connections (wiring)
7 and/or components (circuits) made from highly conductive materials such as copper and
8 gold that are connected to bonding lands 20' and 20''.

9 An uncured film 30, made in accordance with the instant invention, is then die cut to
10 a size that is slightly smaller than the chip 40 that is going to be attached to the PB 10. The
11 uncured film 30 has a thickness that is slightly thicker than the desired chip/PB separation.
12 The sizing and thickness of the uncured film 30 is critical toward insuring that the film's
13 volume is sufficient to make the underfill and flow about the bonds without flowing outside
14 the bonding area on the surface of the PB 10. The uncured film 30 is manually or
15 mechanically placed between the bonding land 20' and 20'' on the PB 10. Mechanical
16 placement is obviously favored in order to insure accuracy and consistency in the procedure.

17 A silicon chip 40 is then provided. Solder bumps 50' and 50'' are placed over the
18 I/O's on the chip 40. These solder bumps may be formed from a variety of known solders.
19 For example a tin/lead mixture that reflows between 200°C and 240°C may be utilized. This
20 is the type of solder that is generally used for in-house electronic applications. Additionally,
21 a tin lead mixture that contains a high concentration of lead (~95%) and reflows around
22 325°C can be used. This is the type of solder that is generally used by the automotive
23 industry for high heat applications.

24 The chip 40 containing solder bumps 50' and 50'', is then lowered onto the uncured
25 film 30 so that the solder bumps 50' and 50'' align with bonding lands 20' and 20'' on the
26 PB 10. Sandwiched between the chip 40 and PB 10 is the uncured film 30.

27 The entire assembly is then subjected to heat and pressure. The heat and pressure
28 cause the uncured film 30 to flow to the edges of the assembly. Simultaneously, the solder
29 bumps 50' and 50'' descend to contact the bonding lands 20' and 20''. The heat and
30 pressure parameters are selected to so that the uncured film 30 cures simultaneously with the
31 formation of the solder joints 75' and 75''. In a typical application, cure is effected at a

1 temperature around 325°C (which is the solder reflow temperature of tin/lead solder
2 mixtures having a high lead content). Typically, no pressure is needed. The time necessary
3 to fully cure the material is generally less than 2.5 minutes and, most preferably, is less than
4 30 seconds.

5 The final product is an underfilled circuit assembly 60 wherein the cured film 70 fills
6 the entire area around and between the solder joints 75' and 75". The underfilled circuit
7 assembly 60 comprises a chip 40 whose I/O's are bonded by solder bumps 50' and 50" to
8 bonding leads 20' and 20" on the PB 10. The chip 40 is further adhered to the PB 10 by a
9 cured underfill film 70 that fills the separation between the chip and the PB 10.

10 FIG. 2 illustrates the desired geometry of the cured film 70 which forms the
11 adhesive bond in the underfilled circuit assembly 60. In FIG. 2, an underfilled circuit
12 assembly 60 is split by a center line 80. The illustrated left half of the underfilled circuit
13 assembly 60 comprises a PB 10 containing a bonding land 20 attached by a solder joint 75 to
14 a chip 40. The area around the solder joint 75 is filled by a cured film 70. A concave fillet
15 85 at the edge of the assembly 60 is formed by excess film 70 which flowed and cured
16 outside of the joint 75. A well shaped and sized fillet 85 will improve the adhesive
17 properties of the bond.

18 One of the benefits of the aforementioned process is that the chips are underfilled in
19 a very short time frame. Furthermore, since the size of the underfill films are cut to closely
20 approximate the size of the chips, the impact of increasing chip size on production time is
21 eliminated. An additional benefit of the technology is that the films cure concurrently with
22 the soldering of the chips to the PB. Thus the separate cure cycle required by the state of the
23 art liquid underfill materials is eliminated. Finally, the technology demonstrates improved
24 durability. The underfills have been tested to 5000 cycles before failure compared to the
25 2000 thermal cycles characteristic of liquid systems.

26 The following examples are illustrative of the invention:

27 Example 1

28 The superiority of matrix soluble curing agents over matrix insoluble curing agents
29 for underfilling can be observed by Differential Scanning Calorimetry (DSC) measurements
30 taken during cure. DSC measurements were taken at temperatures up to 200°C (the limit of
31 the instrument) for three samples of an epoxy resin. The three samples were identical in

every way with the exception that each sample contained a different curing agent. The three curing agents tested were as follows:

(1) 1-cyanoethyl-2-ethyl-4-methylimidazole (CURIMID CN), a liquid imidazole that is soluble in the epoxy resin at room temperature;

(2) 4,4'-diaminodiphenylsulfone/ dicyandiamide (DDS/Dicy); an aromatic amine that is soluble in the epoxy resin at low temperatures (greater than room temperature but less than 100°C); and

(3) 2-methylimidazole Azine (2MZ-Azine), a latent curing agent that is insoluble in the epoxy resin at low temperatures.

FIG. 3 sets forth the data obtained from this experiment. FIG. 3 plots the heat of reaction, in Kcal/eq, for each of the three systems; versus the heating rate, in degrees Celsius. As can be seen, CURIMID CN generates ~85% of the theoretical epoxy heat of reaction (which is around 25 Kcal/eq) at 10°C/min and retains ~70% of this value when cured at 200°C/min. The aromatic amine system, 4, 4'-DDS/Dicy generates 100% of the theoretical heat of reaction when heated at 10°C/min and retains 85% of this value when heated at 200°C/min. However, 2-methylimidazole (2MZ-Azine), the insoluble imidazole curing agent exhibits a very low heat of reaction (~40% of the theoretical) both at high and low heating rates.

Additional tests were run on various catalysts in an Epon 828 epoxy system. The tests are summarized in the following Table 1:

TABLE 1

Curing Agent	Melting Point (°C)	Concentration (Mol/eq epoxy)	Temperature of Cure Onset (°C)	Temperature of Cure Peak (°C)	delta H (Kcal/eq epoxy)
2-ethyl-4-methyl imidazole	<25	3.38E-02	113.3	121.0	14.9
		6.76E-02	110.9	119.0	20.0
1-2-(diamino triazine)-ethyl-2-methyl imidazole	248	3.40E-02	152.6	161.3	9.3
		6.79E-02	152.8	158.5	13.9
1-benzyl-methyl imidazole	<25	6.77E-02	123.5	139.0	20.8

1	benzimidazole	173	6.70E-02	157.0	186.0	8.3
2	2-mercapto-	303	6.70E-02	146.0	167.0	0.9
3	benzimidazole					
4	1-(2-	<25	3.42E-02	126.7	148.7	9.2
5	cyanoethyl)-2-		6.72E-02	130.1	141.8	20.9
6	ethyl-4-methyl					
7	imidazole					
8	Isophthalic	>>25	2.00E-01	190.4	196.2	17.1
9	acid		2.50E-01	188.9	193.8	17.3
10	dihydrazide					
11	4,4'-diamino-	176/209	1.443E-01/	154.2	200.6	28.0
12	diphenyl		2.875E-01			
13	sulfone/					
14	dicyano-					
15	diamide					

16
17 The room temperature soluble catalysts in Table 1 are 2-ethyl-4-methylimidazole, 1-
18 benzyl-2-methylimidazole and 1-(2-cyanoethyl-ethyl-4-methylimidazole. The low
19 temperature soluble catalysts (soluble at less than 100°C) in the table are bis 4,4'-
20 diaminodiphenylsulfone/dicyandiamide and isophthalic acid dihydrazide. The insoluble
21 catalysts in the table are 1-2(diaminotriazine)ethyl-2-methylimidazole, benzimidazole, and
22 2-mercaptobenzimidazole. Once again, the room temperature and low temperature soluble
23 catalysts generated heats of reaction greater than 75% of the theoretical value whereas the
24 insoluble catalysts, such as benzimidazole generated significantly lower heats of reaction.

25 One rationalization for this phenomenon is that the solution and diffusion kinetics of
26 the insoluble materials are slower than the cure kinetics. As a result, a gel layer is formed
27 around the curing agent during cure the inhibits its ability to diffuse throughout the matrix
28 and create a uniformly curing product.

29 Based on this data, only the room temperature soluble imidazole, or low temperature
30 soluble aromatic amines, are preferred curing agents. These curing agents cure the resin in a
31 steady and uniform without generating volatiles that create voids. In contrast, test films
32 made using the latent, insoluble imidazole as a curative contained a high content of voids.

33 Example 2

34 The cure kinetics of the underfill film is critical to its success. As stated, during
35 cure, the film should exhibit a heat of reaction that is, most preferably, 90% of the

1 theoretical heat of reaction when tested at heating rate of 10°C/min, and that is 70% of the
2 theoretical heat of reaction when tested at a heating rate of 200°C/min. Room temperature
3 soluble curing agents are best able to meet the requisite cure kinetics. To demonstrate this
4 point, the high temperature curing rates of two films from Example 1 were measured.
5 Specifically, two identical epoxy resins, one containing the room temperature soluble
6 imidazole 1-cyanoethyl-2-ethyl-4-methylimidazole (CURIMID CN) and the other containing
7 the low temperature soluble 4,4'-diaminodiphenylsulfone/ dicyandiamide (DDS/Dicy), were
8 tested. The data obtained is set forth in FIG. 4.

9 **FIG. 4** graphs the peak reaction temperature in degrees Celsius versus the log of the
10 heating rate for the two films. As can be seen, the room temperature soluble imidazole
11 system is the fastest curing system. It generates the lowest peak reaction temperature at the
12 same heating rate. In contrast, the aromatic amine system is the slowest system,
13 demonstrating a peak reaction temperature of 70°C or more greater than the soluble
14 imidazole. Underfill processing problems arise when slower curing compositions are used
15 because the composition does not fully cure in the short time it takes to reach the processing
16 temperature. Large voids are then produced due to volatilization of the uncured resin.

17 Room temperature soluble catalysts are, therefore, the preferred curing agent for use
18 in the invention. These catalysts generally, and room temperature imidazoles specifically,
19 cure more fully in the same amount of time and generate fewer volatiles. As a result, the
20 products exhibit fewer voids. In contrast, test specimens made using the aromatic amine
21 curing agent generated a higher void content.

22 **Example 3**

23 The particle size of the fillers employed in the underfill film is critical to its ability to
24 ensure electrical continuity within the solder joints. The particle size distribution is chosen
25 so that the descending solder ball can push the filler away from the solder joint and, thereby,
26 prevent the filler from getting caught between the solder ball and the bonding pad. Filler
27 caught between the solder ball and bonding pad can disrupt the electrical continuity of the
28 bond.

29 To demonstrate this phenomenon, two filler mixes of different particle size
30 distributions were added to two identical samples of an epoxy resin composition. The
31 particle size distributions of two filler mixes is set forth in FIG. 5. Also shown in FIG. 5 is

the 25 μm bump spacing that represents the typical separation between solder joints in an integrated circuit assembly.

As can be seen, the first filler mixture has a median particle size of approximately 25 μm . The resultant underfilled chip exhibited low levels of circuit continuity. Microscopic examination of these assemblies showed that the larger filler particles were being trapped at or near individual solder bumps, precluding bonding of these bumps to the associated PB bonding land. These portions of the circuits, of course, did not exhibit any electrical continuity.

The second filler mixture has a median particle size of approximately 4 to 5 μm . Underfilled chips using this filler mix exhibited 100% circuit continuity. Microscopic examination of the underfilled chips showed that the filler, in this case, "flowed" around and away from the solder bumps, allowing all solder joints to be successfully bonded.

The significant difference between these two filler packages is the size and proportion of the largest particle size fillers. The smallest distribution filler package is greater than 90% less than the 25 μm bump spacing and 100% less than 30 μm . In contrast, the unsuccessful filler blend has a maximum particle size of 80-90 μm and 10% are greater than 50 μm .

Example 4

To demonstrate typical formulations that will and will not work in the instant invention, a variety of films were prepared and tested. The ratio and type of ingredients used in these films set forth in Table 2 below:

TABLE 2

Ingredients	Comp A (wt%)	Comp B (wt%)	Comp C (wt%)	Comp D (wt%)	Comp E (wt%)	Comp F (wt%)	Comp G (wt%)
Phenoxy PKHH ¹						1.37	1.36
Epon 828 ²	8.5						
Tactix 742 ³	12.7						
Tactix 695 ⁴	12.7						
Epon 164 ⁶					7.95		

Ingredients	Comp A (wt%)	Comp B (wt%)	Comp C (wt%)	Comp D (wt%)	Comp E (wt%)	Comp F (wt%)	Comp G (wt%)
1 Epicion 2 830S ⁷	5.6						
3 ECN 1873 ⁸				10.61		5.88	5.83
4 RSL 1462 ⁹					11.93	9.81	9.71
5 DEN 438 ¹⁰	0.8	21.10	23.33	23.09			
6 MY0500 ¹¹			5.43	7.51			
7 Epon 8 1001F ¹²						3.92	3.88
9 PC 1344 ¹³		0.15	0.10		0.12	0.12	0.12
10 Blendex 11 311 ¹⁴	8.5	4.86	5.37	7.90			
12 X5-8452 ¹⁵					1.99	1.96	1.94
13 Novacite 14 550 ¹⁶	42.3			39.47			
15 Teco-Sil 16 200F ¹⁷		62.34	51.56				
17 GP-31 ¹⁸			5.74				
18 FB-74 ¹⁹					57.32	56.54	
19 FB-6S ²⁰					19.11	18.85	63.45
20 FB-3S ²¹							11.19
21 TS 720 ²²	2.6	0.77	1.68	2.37	0.60	0.59	0.59
22 4,4'-DDS ²³	5.4	5.02	5.81				
23 Dicy ²⁴	0.9	0.85	0.98				
24 IPDH ²⁵				9.05			
25 2MX- 26 Azine ²⁶					0.99		
27 Curimide 28 CN ²⁷						0.96	0.96

Ingredients	Comp A (wt%)	Comp B (wt%)	Comp C (wt%)	Comp D (wt%)	Comp E (wt%)	Comp F (wt%)	Comp G (wt%)
Color Dispersion ²⁸							0.97
Total	100.00	100.00	100.00	100.00	100.01	100.00	100.00
% Filler	44.9	63.11	58.98	41.84	77.03	75.98	75.23

¹Phenoxy PKHH is a high molecular weight bisphenol A epoxy manufactured by Phenoxy Associates.

²Epon 828 is a liquid bisphenol A epoxy resin manufactured by Shell Chemical.

³Tactix 742 is a trifunctional epoxy resin manufactured by Ciba.

⁴Tactix 695 is a toughened multifunctional epoxy resin manufactured by Ciba.

⁵Epon 164 is an epoxidized cresol novolac manufactured by Shell.

⁶Epichlon 830S is a liquid bisphenol F epoxy resin manufactured by Dainippon.

⁷ECN 1873 is an epoxidized cresol novolac manufactured by Ciba.

⁸RSL 1462 is a liquid bisphenol A epoxy resin manufactured by Shell.

⁹DEN 438 is an epoxidized phenol novolac manufactured by Dow.

¹⁰MY 721 is an epoxidized methylene dianiline manufactured by Ciba.

¹¹MYO500 is a triglycidyl-para-aminophenol manufactured by Ciba.

¹²Epon 1001F is a solid bisphenol A epoxy manufactured by Shell.

¹³PC 1344 is a nonionic surfactant manufactured by Monanto.

¹⁴Blendex 311 is an ABS toughener manufactured by General Electric.

¹⁵X5-8452 is a silicone toughener manufactured by Dow Corning.

¹⁶Novocite 550 is an electronics grade silica produced by Malvern.

¹⁷Teco-Sil 200F is an electronics grade silica produced by Combustion Engineering.

¹⁸GP-31 is an electronics grade silica produced by Harbison Walker.

¹⁹FB-74 is an electronics grade silica produced by Denka.

²⁰FB-6S is an electronics grade silica produced by Denka.

²¹FB-3S is an electronics grade silica produced by Denka.

²²TS 720 is a fumed silica thixotrope produced by Cabot.

²³4,4'-DDS is a diaminodiphenylsulfone produced by Ciba.

²⁴Dicy is a dicyandiamide produced by Air products.

²⁵2MX-Azine is a 2-methylimidazole-azine produced by Air Products.

²⁶Curimid CN is a 1 cyanoethyl-2-ethyl-4-methylimidazole produced by PolyOrganix.

²⁷Color Dispersion is a phthalocyanine pigment/epoxy milled dispersion available from a variety of manufacturers.

Compositions E and G form high viscosity films that have proven useful in the instant invention. Compositions A, C and D should also form high viscosity films that are useful in the instant invention. Compositions B and F are compositions that have been proven ineffective for use in the instant invention.

The properties of each of the aforementioned compositions A through F were examined. The results of this examination are set forth in Table 3 below:

TABLE 3

Property	Comp A	Comp B	Comp C	Comp D	Comp E	Comp F	Comp G
Minimum Viscosity, (poise)	505	1080	3150	2940	302	2100	1000
Minimum Viscosity Temp. (C)	148	125	Not Tested	Not Tested	120	111	98.4
DSC Peak Reaction Temp (C)	203	199	202	189	147.3	128.9	132
Heat of Reaction, (Kcal/eq)	16.7	28	20.3	17.1	17.5	20.5	17.5
Tg, ex DMTA (C)	186	204	201	208	162.5	163	159
Underfill Film Thickness	Not Tested	Good	Not Tested	Not Tested	Good	Good	Good
Underfill Flow	Not Tested	Good	Not Tested	Not Tested	Good	Not sufficient	Good
Underfill Cure Speed	Not Tested	Too Slow	Not Tested	Not Tested	Slow	Good	Good
Underfill Voiding	Not Tested	Gross	Not Tested	Not Tested	Moderate	None	None

The thermal cycle resistance of a film substantially identical to Composition G was also compared with a commercially available low viscosity underfill composition (Dexter FP4450). The resultant data is set forth in Table 4 below:

TABLE 4

PROPERTY	Dexter FP4450	Underfill film (from Table 1)
Form	Low Viscosity Liquid	High Viscosity Film

PROPERTY	Dexter FP4450	Underfill film (from Table 1)
Film Thickness, μm	Not Applicable	75 to 100 μm
viscosity, poise, at 25°C at 45°C at 75°C at 100°C	Brookfield Viscometer 530 40 Not Measured Not Measured	Rheometrics RDA Viscometer Not Measured Not Measured 84400 20550
Cure Schedule	0.5 hr at 125°C + 1.5 hr at 165°C	30 sec at 325°C
Tg, °C	160°C	162°C
CTE, ppm/°C alpha 1 alpha 2	18 72	23 74
Thermal Cycle, Cycles to Failure -55°C to 150°C	2000	5000

As is evident from Table 4, composition G, which is a high viscosity composition comprising an epoxy phenol novolac, asolid bisphenol epoxy and a liquid bisphenol epoxy, exhibits a 250% improvement in thermal cycle resistance when compared to the commercial liquid underfill.

5 While the invention has been described in conjunction with the specific embodiments outlined above, it is evident that many alternatives, modifications, and variations will be apparent to those skilled in the art. Accordingly, the preferred embodiments of the invention are intended to be illustrative and not limiting. Various changes may be made without departing from the spirit and scope of the invention as

10 defined in the claims.

CLAIMS

1. An uncured and unreinforced film comprising: (a) 0.5 to 50%, by weight of the film, of a polymeric or polymer forming matrix material; (b) 0.01 to 10%, by weight of the film, of a curing agent that is soluble in the matrix material at a temperature no greater than 100°C; and (c) 50 to 80%, by volume of the film, of a substantially spherical and inert filler that has a maximum particle size no greater than 30 μm ,
5 wherein said film possesses the following physical and kinetic characteristics: (i) a smooth, uninterrupted surface; (ii) a uniform thickness of 5 mils or less with a deviation of ± 0.5 mils or less and a Cpk higher than 1.0; (iii) a viscosity of at least 50,000 poise at room temperature; (iv) sufficiently low tack to permit die-cutting and machine placement; (v) sufficient flexibility to be handled without breaking; (vi) an activation energy no greater than 300 KJ/mol; and the ability to retain more than 50% of its theoretical heat of reaction when tested at a heating rate of 200°C/min.
- 15 2. The film of claim 1, wherein the matrix material is selected from the group consisting of epoxy resins, cyanate ester resins, bismaleimide resins, vinyl resins, phenoxy resins, polyethersulfones, polyphenyleneoxides, polyesters, polyimides, polyamides, and polyurethanes.
3. The film of claim 1, wherein the matrix material is an epoxy resin.
- 20 4. The film of claim 1 wherein the matrix material is an anhydride hardener free epoxy resin composition that comprises: a novolac epoxy; a liquid bisphenol epoxy; and a solid bisphenol epoxy.
5. The film of claim 1 wherein the curing agent is soluble in the matrix material at room temperature.
- 25 6. The film of claim 1 wherein the curing agent is an imidazole.
7. The film of claim 1 wherein the filler is selected from the group organic and inorganic fillers that are insoluble in the matrix material and have a coefficient of thermal expansion (CTE) that is less than 10 ppm/°C.
8. The film of claim 1 wherein the filler is a silica filler.
- 30 9. The film of claim 1 wherein the filler is present in a volume fraction of 63 to 80%.

10. The film of claim 1 wherein the filler is present in a volume fraction of 63 to 72%.

11. The film of claim 1 wherein the filler has a maximum particle size less than or equal 12.5 μm .

5 12. The film of claim 1 wherein the filler has a maximum particle size less than or equal 8.25 μm .

13. The film of claim 1 wherein the film has a thickness of 3-4 mils with a variation of ± 0.5 mils or less and a Cpk greater than 1.0.

10 14. The film of claim 1 wherein the film has a thickness of 3-4 mils with 3 sigma variation of ± 0.5 mils or less and a Cpk greater than 1.0 and wherein the film comprises: (a) 0.5 to 50%, by weight of the film, of an epoxy resin; (b) 0.01 to 10%, by weight of the film, of an imidazole curing agent that is soluble in the matrix material at room temperature; (c) 63 to 80%, by volume of the film, of a substantially spherical and inert filler hat has a maximum particle size no greater than 30 μm .

15 15. The film of claim 1 wherein the film has a thickness of 3-4 mils with a variation of ± 0.5 mils or less and a Cpk greater than 1.0 and wherein the film comprises: (a) 0.5 to 50%, by weight of the film, of a matrix material that comprises a novolac epoxy; a liquid bisphenol epoxy; and a solid bisphenol epoxy; (b) 0.01 to 10%, by weight of the film, of an imidazole curing agent that is soluble in the matrix material at room temperature; (c)
20 63 to 80%, by volume of the film, of a substantially spherical and inert filler hat has a maximum particle size no greater than 30 μm .

16. The film of claim 1, wherein the film is attached to one or more release layers that can be pulled away from the film immediately prior to use.

25 17. A cured film formed by curing the uncured film in claim 1, wherein said cured film is void free, has a coefficient of thermal expansion (CTE) between 20 and 25 ppm/ $^{\circ}\text{C}$, has an isotropic modulus, fracture strength, CTE and thermal conductivity, and has a thermal cycle resistance sufficient to withstand more than 2,000 thermal cycles.

18. The cured film of claim 17 wherein the cured film has at thermal cycle resistance sufficient to withstand 5,000 thermal cycles.

30

19. A process for furthering the adhesion between a chip and a printed board and, simultaneously, filling the separation between the chip and the printed board, comprising the following steps:

(1) providing an uncured and unreinforced film that comprises: (a) 0.5 to 50%,
5 by weight of the film, of a polymeric or polymer forming matrix material; (b) 0.01 to 10%,
by weight of the film, of a curing agent that is soluble in the matrix material at a temperature
no greater than 100°C; and (c) 50 to 80%, by volume of the film, of a substantially spherical
and inert filler that has a maximum particle size no greater than 30 μm ,

wherein said film possesses the following characteristics: (i) a smooth, uninterrupted
10 surface; (ii) a uniform thickness of 5 mils or less with a deviation of ± 0.5 mils or less and a
Cpk higher than 1.0; (iii) a viscosity of at least 50,000 poise at room temperature; (iv)
sufficiently low tack to permit die-cutting and machine placement; (v) sufficient flexibility
to be handled without breaking; (vi) an activation energy no greater than 300 KJ/mol; and
the ability to retain more than 50% of its theoretical heat of reaction when tested at a heating
15 rate of 200°C/min;

(2) die cutting said film to obtain a cut film that is smaller than the chip to be
bonded and thicker than the final separation between the soldered chip and the printed
board;

(3) mechanically placing said cut film between two or more bonding lands on the
20 printed board or, alternatively, mechanically placing said cut film between two or more
input/output points on the surface of the chip;

(4) attaching solder bumps onto the input/output points on the surface of the
chip;

(5) positioning the chip next to the printed board so that the cut film lies between
25 the chip and the printed board and the solder bumps on the chip align with the bonding lands
on the printed board; and

(6) applying heat and/or pressure sufficient to cause the solder to fully descend
onto the bonding lands and form solder joints and, simultaneously, cause the uncured film to
flow around and between the solder joints and cure, thereby, creating a cured film that aids
30 the adhesion of the soldered chip to the printed board and, simultaneously, filling the
separation between the chip and the printed board.

20. The process of claim 19 wherein said cured film is void free, has a coefficient of thermal expansion (CTE) between 20 and 25 ppm/°C, has an isotropic modulus, fracture strength, CTE and thermal conductivity, and has a thermal cycle resistance sufficient to withstand more than 2,000 thermal cycles.

5 21. The cured film of claim 20 wherein the cured film has at thermal cycle resistance sufficient to withstand 5,000 thermal cycles.

22. An assembly comprising:

(I) a printed board;

(II) a chip; and

10 (III) a cured film that adheres the chip to the printed board and completely fills the separation between the chip and printed board,

wherein said cured film is void free, has a coefficient of thermal expansion (CTE) between 20 and 25 ppm/°C, has an isotropic modulus, fracture strength, CTE and thermal conductivity, and has a thermal cycle resistance sufficient to withstand more than 2,000 thermal cycles,

15 and wherein said cured film is formed by curing an uncured film comprising the following components:

(a) 0.5 to 50%, by weight of the film, of a polymeric or polymer forming matrix material; (b) 0.01 to 10%, by weight of the film, of a curing agent that is soluble in the matrix material at a temperature no greater than 100°C; and

20 (c) 50 to 80%, by volume of the film, of a substantially spherical and inert filler that has a maximum particle size no greater than 30 µm.

23. The cured film of claim 22 wherein the cured film has at thermal cycle resistance sufficient to withstand 5,000 thermal cycles.

Illustration of Underfill Process

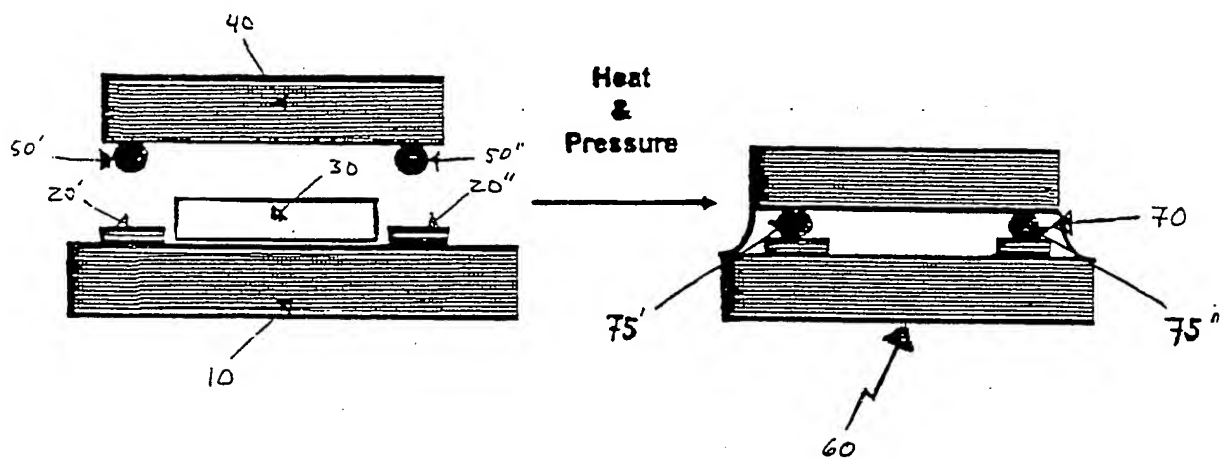


Figure 1

Underfill Film

Desired Geometry of Cured Adhesive Bond

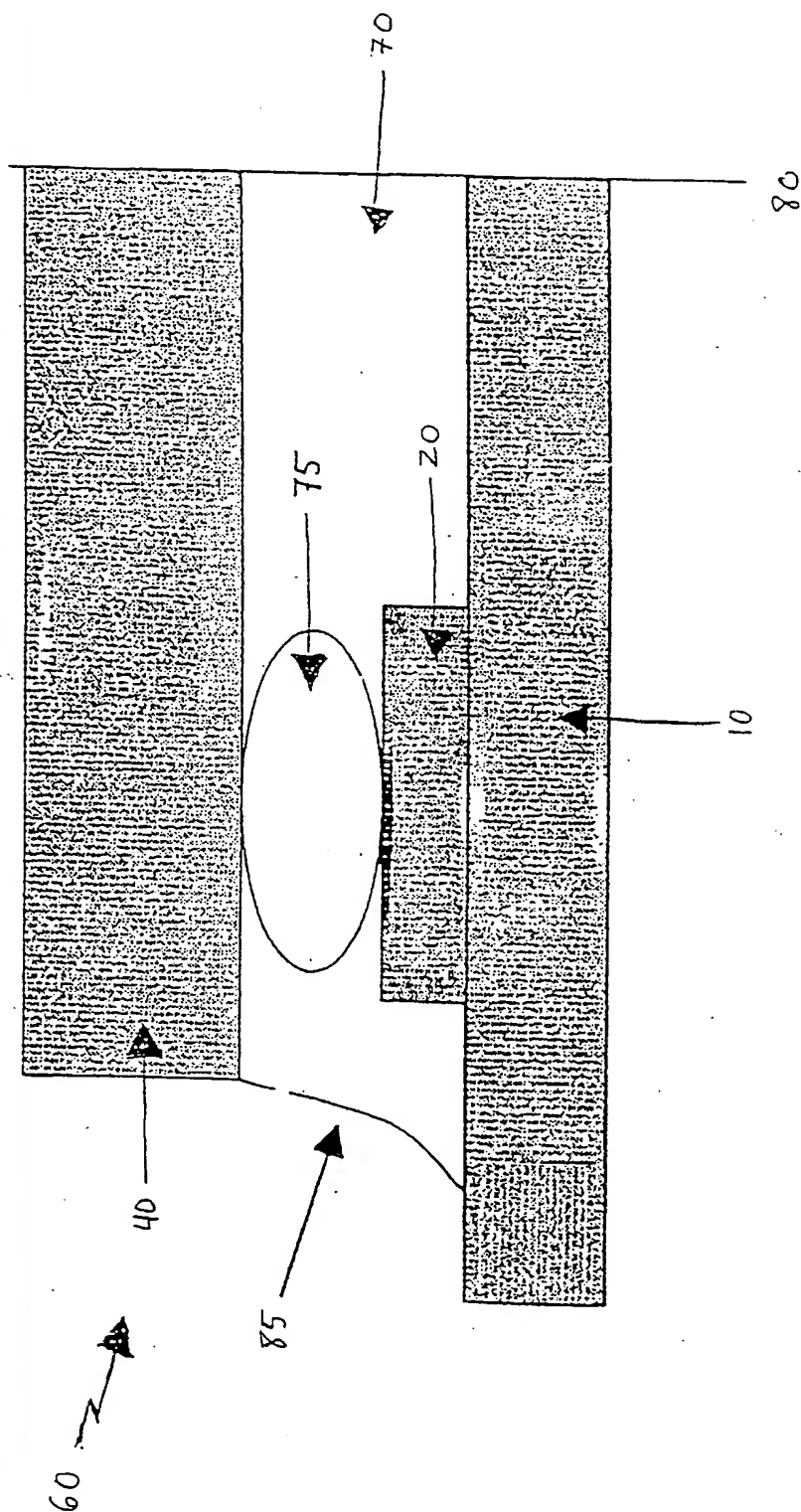


Figure 2

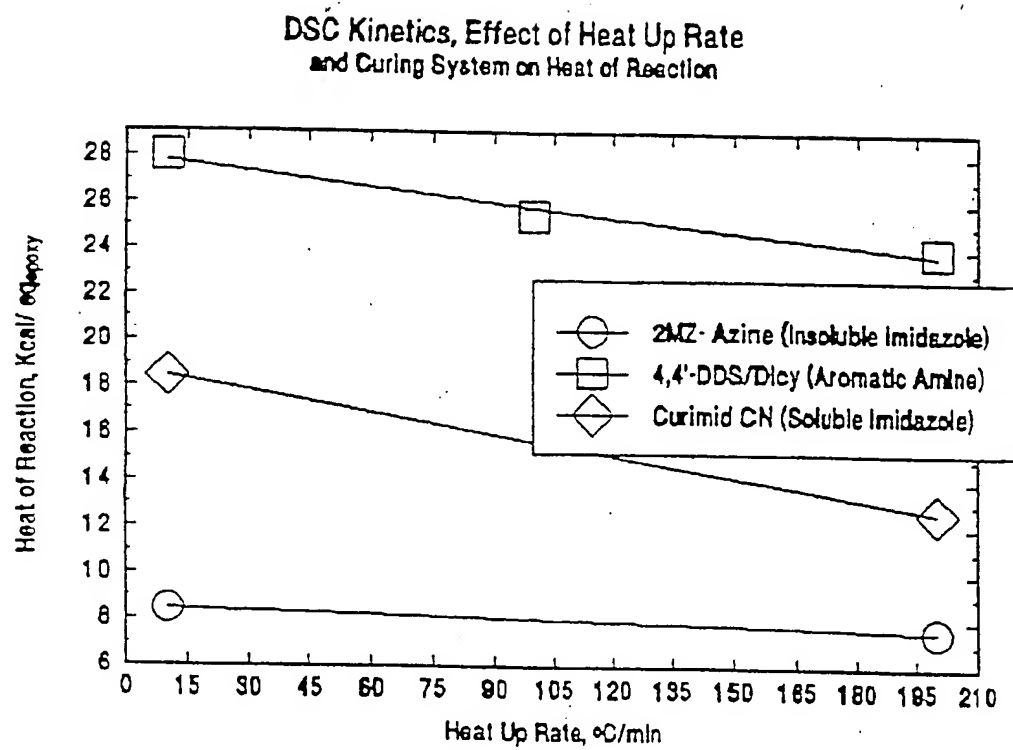


Figure 3

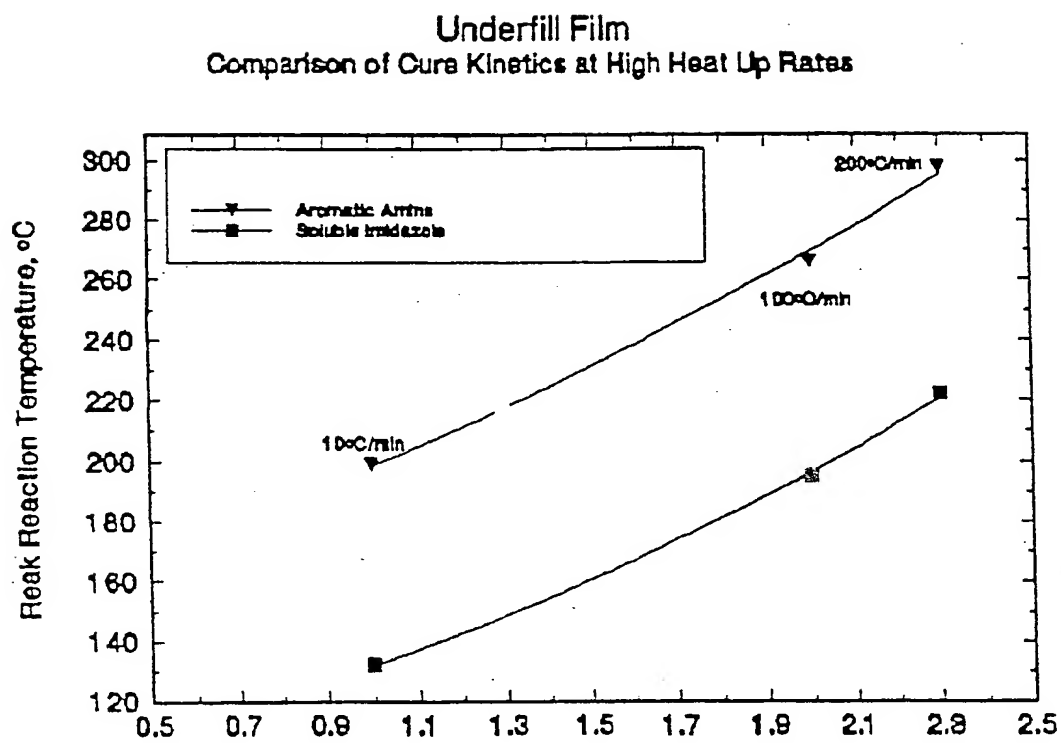


Figure 4

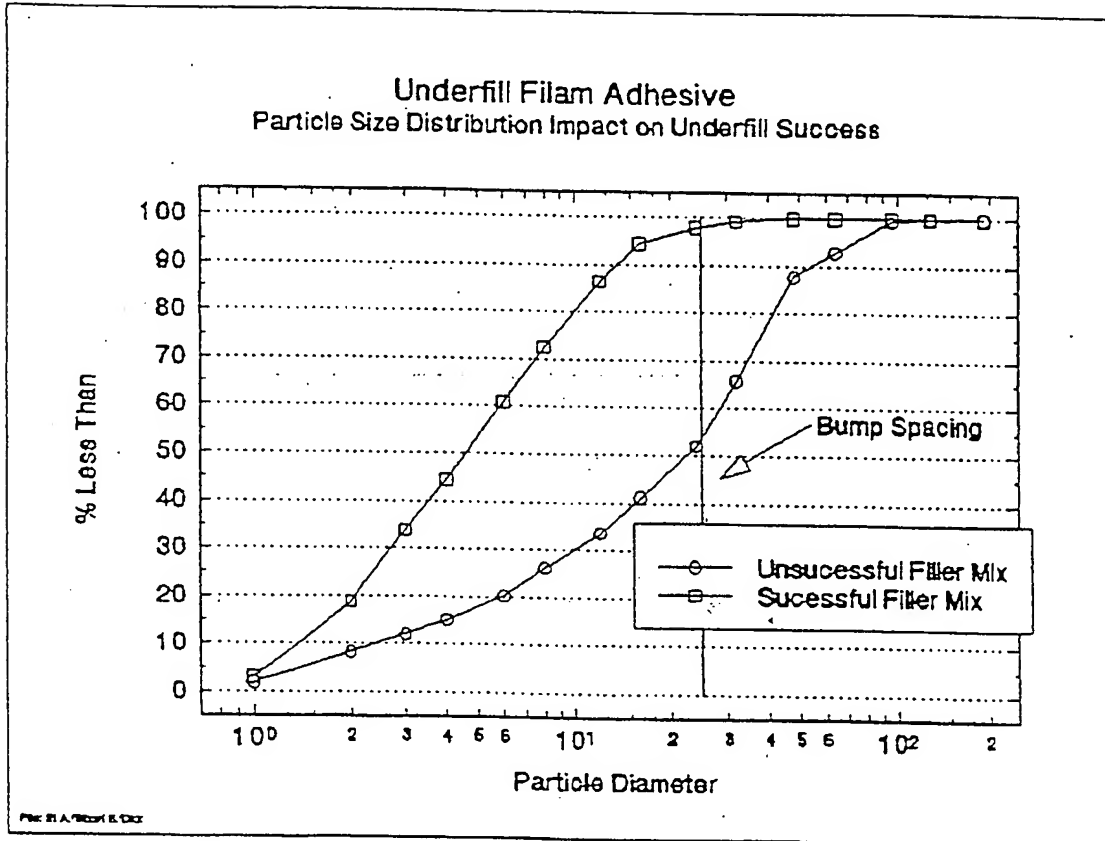


Figure 5

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/28768

A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : Please See Extra Sheet.

US CL : Please See Extra Sheet.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 156/307.7, 330; 257/788, 789, 792, 793; 361/783; 428/349, 355EP; 438/108, 118, 127; 523/429, 443

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

WEST-USPT, EPAB, JPAB, DWPI (search terms: underfill, encapsulant, epoxy resin and species of polymers defined in claim 4, viscosity, (centi)poise, die cut)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,386,624 A (GEORGE et al.) 07 February, 1995, column 2, lines 15-21 and column 4, lines 33-40.	1-23
P, Y	US 5,972,739 A (FUNADA et al.) 26 October 1999, column 6, lines 30-37 and column 8, lines 1-6.	1-23
P, Y	US 5,918,113 (HIGASHI et al.) 29 June 1999, column 2, lines 33-41 and column 3, lines 49-60.	1-23
Y	JP 10-125825 A (NEC CORP) 15 May 1998, abstract.	1-23
Y	US 4,437,235 A (MCIVER) 20 March 1984, column 4, lines 4-16 and 22-29.	1-23

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
B earlier document published on or after the international filing date	*Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A* document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means	
P document published prior to the international filing date but later than the priority date claimed	

Date of the actual completion of the international search

21 MARCH 2000

Date of mailing of the international search report

31 MAR 2000

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/28768

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5,814,401 A (GAMOTA et al.) 29 September 1998, column 2, lines 34-41 and 60-65; and column 3, lines 6-8, 17-23 and 31-50.	1-23
Y	US 5,391,924 A (UCHIDA et al.) 21 February 1995, column 2, lines 16-26; column 4, lines 3-13; column 5, lines 18-22 and 45-47; and column 7, lines 22-31.	3, 4 and 7-12
Y	US 5,248,710 (SHIOBARA et al.) 28 September 1993, column 5, lines 16-39.	7-12

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/28768

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

Please See Extra Sheet.

1. ☒ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐

The additional search fees were accompanied by the applicant's protest.

☒

No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/28768

A. CLASSIFICATION OF SUBJECT MATTER:

IPC (7):

B32B 07/12, 31/26; C08K 03/36, 07/18; C09J 163/02, 163/04; H01L 21/56, 21/58; H05K 07/06

A. CLASSIFICATION OF SUBJECT MATTER:

US CL :

156/307.7, 330; 257/788, 789, 792, 793; 361/783; 428/349, 355EP; 438/108, 118, 127; 523/429, 443

BOX II. OBSERVATIONS WHERE UNITY OF INVENTION WAS LACKING

This ISA found multiple inventions as follows:

This application contains the following inventions or groups of inventions which are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for all inventions to be searched, the appropriate additional search fees must be paid.

Group I, claims 1-21, drawn to a film and process of adhering a chip and printed board using the film wherein the film comprises a polymer matrix, a matrix-soluble curing agent and a spherical inert filler.

Group II, claims 22 and 23, drawn to an assembly of a chip adhered to a printed board with a film.

The inventions listed as Groups I and II do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features. The special technical feature is the blend of a polymer matrix, a matrix-soluble curing agent and a spherical inert filler. Christie et al (column 7, Example 1) shows a mixture of an epoxy resin, an anhydride curing agent soluble in the epoxy resin and a silica filler.

Accordingly, the claimed blend does not make a contribution over the prior art which substantiates a lack of unity between the inventions.

This application contains claims directed to more than one species of the generic invention. These species are deemed to lack Unity of Invention because they are not so linked as to form a single inventive concept under PCT Rule 13.1. In order for more than one species to be searched, the appropriate additional search fees must be paid. The species are as follows:

(a) The polymer matrices and (b) the curing agents.

The claims are deemed to correspond to the species listed above in the following manner:

Claims 3, 4, 14 and 15 contain species of polymer matrix (a).

Claims 6, 14 and 15 contain species of curing agent (b).

Claims 1-13 and 16-23 are generic.

The species listed above do not relate to a single inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, the species lack the same or corresponding special technical features for the following reasons:

The polymer matrix embraces bismaleimides, cyanate ester resins, epoxy acrylate resins and epoxy resins which are functionally and structurally distinct polymers conferring distinct physical properties to the film.

The curing agents are specific to the particular polymer matrix (description, page 16, line 8 to page 17, line 25) and encompass a variety of functionally and structurally diverse compounds which react differently with the functional groups of the polymer matrix to yield structurally distinct cured products.

Applicants' attorney W. Robinson H. Clark during a telephonic response to the lack of unity of invention on March 14, 2000 elected to pay for the examination of the two additional inventions (as corroborated by the submission of the \$420 fee via fax on March 14, 2000) and elected epoxy resin mixture of claim 4 as matrix material (a) and the imidazole of claim 6 as the curing agent (b).

